SILICONE COMPOUNDS HAVING STERICALLY HINDERED CYCLIC AMINE FUNCTIONS AND COMPATIBILIZING FUNCTIONS, AND USE THEREOF FOR LIGHT- AND HEAT-STABILIZATION OF POLYMERS
[COMPOSES SILICONE A FONCTIONS AMINES CYCLIQUES STERIQUEMENT ENCOMBREES ET A COMPATIBILISANTES ET LEUR UTILISATION DANS LA STABILISATION LUMIERE ET THERMIQUE DES POLYMERES]

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# SILICONE COMPOUNDS HAVING STERICALLY HINDERED CYCLIC AMINE FUNCTIONS AND COMPATIBILISING FUNCTIONS, AND USE THEREOF FOR LIGHT AND HEAT STABILISATION OF POLYMERS

This invention relates primarily to new mixed silicone compounds containing in their structure sterically hindered cyclic amine functions bound to silicon atoms via Si-O-C or Si-alkylenecarbonyloxy-C bonds and other functions bound to silicon via compatibilizing Si-C bonds. It secondarily relates to processes for preparing these silicone compounds. Thirdly it relates to the use of such compounds in polymers to improve their resistance under the effects of ultraviolet radiation, ambient oxygen and heat.

In fact, organic polymers and more particularly polyolefins and polyalkadienes undergo deterioration when subjected to external agents and in particular the combined action of air and solar ultraviolet radiation.

This deterioration is generally limited by the addition of small quantities of stabilizing agents to the polymer.

Among these anti-UV stabilizers, sterically hindered amines, in particular tetramethyl-2,2,6,6 piperidines, are the most effective.

However, in practice, one of the major problems relating to use of these anti-UV stabilizers is obtaining a good compromise between their efficacy, which requires that they be mobile within the polymer, and the duration of their action, which requires use of molecules with a high molecular mass having high compatibility with the polymers to be stabilized.

<sup>\*</sup> Number in the margin indicates pagination in the foreign text.

It was proposed in the prior art that polyorganosiloxanes having sterically hindered piperidinyl functions could be used advantageously. As documents illustrating this prior art, we can cite for example the following documents: JP-A-01/096259, EP-A-0 338393, EP-A-0 343717, EP-A-0 358190, EP-A-0 388321 and EP-A-0 491659. In these documents, polyorganosiloxanes having sterically hindered piperidinyl functions are described in which the piperidinyl group could be bound to the silicon atom via a Si-O-C bond (see in particular EP-A-0 343717 and EP-A-0 358190) or a Si-alkylenecarbonyloxy-C bond (see in particular EP-A-0 358190, EP-A-0 388321 and EP-A-0 491659).

While carrying out work in this area of technology, the /2 applicant found new mixed polyorganosiloxanes having on the one hand statically hindered amine function(s) bound to silicon via a single Si-O-C or Si-alkylenecarbonyloxy-C bond and on the other hand particular function(s) with a compatibilizing action bound to silicon via a Si-C bond, which have properties useful for improving the resistance of polymers to deterioration under the effects of UV radiation, ambient oxygen and heat.

More specifically, this invention primarily relates to polyorganosiloxanes containing at least 3 siloxyl units per molecule, including:

- at least one functional siloxyl unit having the formula:

$$(R)_a x si(0)_{\underbrace{3a}_2}$$

Wherein:

- symbols R<sup>1</sup> are identical or different and represent a monovalent hydrocarbon radical chosen from among the linear or branched alkyl radicals, having from 1 to 4 atoms of carbon and phenyl;
- the symbol X represents a monovalent group having formula -A-Z where:
  - A is a divalent radical chosen from among an oxygen atom and a radical having formula -CH<sub>2</sub>-CHR<sup>2</sup>-COO- with R<sup>2</sup> being a hydrogen atom or an linear or branched alkyl radical having from 1 to 3 carbon atoms, the free valency of the carbon atom being bound to the silicon atom;
  - the symbol Z represents a monovalent group whose free valency is borne by a carbon atom, having a secondary or tertiary amine function, contained in a cyclic hydrocarbon chain having from 8 to 30 carbon atoms, in which the two cyclic carbon atoms situated in positions  $\alpha$  and  $\alpha'$  in relation to the cyclic nitrogen atom do not contain a hydrogen atom;
- a is a number chosen from among 0, 1 and 2; and
   at least one other functional siloxyl unit having the following formula:

# $(R^{\lambda})_b$ WSi(O)<sub>3-b</sub> (II

- symbols R<sup>1</sup> have the same meanings as those given above with regard to formula (I):
- the symbol W represents a monovalent group with a compatibilizing /3 function chosen from among the following: an alkyl linear or branched radical having more than 10 carbon atoms; a radical having formula  $-R^3$ -COO- $R^4$

in which  $R^3$  represents an linear or branched alkylene radical having from 5 to 20 carbon atoms and  $R^4$  represents an linear or branched alkyl radical having from 1 to 12 carbon atoms; a radical having formula  $-R^5-O-(R^6-O)_c-R^7$  in which  $R^5$  represents a linear or branched alkylene radical having from 3 to 15 carbon atoms,  $R^6$  represents a linear or branched alkylene radical having from 1 to 3 carbon atoms, is a number from 0 to 10 and  $R^7$  represents a hydrogen atom, a linear or branched alkyl radical having from 1 to 12 carbon atoms or an acyl radical  $-CO-R^8$  where  $R^8$  represents a linear or branched alkyl radical having from 1 to 11 carbon atoms;

b is a number chosen from among 0, 1 and 2.
 The polyorganosiloxane may also contain at least one other siloxyl unit having the following formula:

$$(R)_{d}(H)_{e}Si(O)_{\underline{4-(d+e)}}$$
 (III)

wherein:

- symbols R<sup>1</sup> have the same meanings as those given above with regard to formula (I):
- d is a number chosen from among 0, 1, 2 and 3;
- e is a number chosen from among 0 and 1;
- the sum d + e is at most equal to 3.

The siloxyl units of formula (I), when there are more than two of them, may be identical or different; the same also applies to siloxyl units of formulas (II) and (III).

In this description, the following definitions shall be used:

- "amine functions": monovalent Z groups not having the A hinge through which they bind to the silicon atoms;
- "compatibilizing functions": monovalent W groups which bind directly to silicon atoms (and so therefore in this case forming Si-C bonds);
- "organopolysiloxanes with oxygen hinge": mixed polymers as claimed in the invention within whose structure the amine functions are bound to the silicon atoms via the A = -O- hinge (in these cases forming Si-O-C bonds);
- "organopolysiloxanes with carboxylate hinge": mixed polymers as claimed in the invention within the structure of which the amine functions are bound to the silicon atoms via the  $A = -CH_2-CHR^2-COO-$

hinge (in these cases forming Si-CH2-CHR2-COO-C bonds).

Given the values that the symbols a, b, d and e may take, it should be further understood that the mixed polyorganosiloxanes as claimed in the invention can then have a linear, cyclic, branched (resin) structure of a mixture of these structures. When it is a matter of linear polymers, these can possibly have up to 50% by mole of branching [units of "T" types  $(RSiO_{3/2})$  and/or "Q"  $(SiO_{4/2})$  types]

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When it is a matter of polyorganosiloxane resins, the latter are composed of at least two types of different siloxyl units, i.e., "M" units"  $(R_3SiO_{1/2})$  and/or "T" units and possibly "D" units  $(R_2SiO_{2/2})$ ; the ratio of the number of "M" units to the number of "Q" and/or "T" units is in general between 4/1 and 0.5/1 inclusive, and the ratio between the number of "D" units to the number of "Q" and/or "T" units is generally between 0 to 100/1 inclusive.

Advantageously, the numbers of units of formulas (I), (II) and possibly (III) are such that the mixed polyorganosiloxanes as claimed in the invention contain the following:

- at least 0.5% by mole, preferably from 10 to 90% by mole, of amine functions,
   and
- at least 0.5% by mole, preferably from 10 to 90% by mole, of compatibilizing functions. The molar percentages indicated express the number of moles of functions for 100 atoms of silicon.

The preferred  $R^1$  radicals are: methyl, ethyl, n-propyl, isopropyl, n-butyl; preferably at least 80% by mole of the  $R^1$  radicals will be methyls.

The preferred carboxylate hinge is chosen from among the divalent radicals -CH2-CH2-COO- and -CH2-CH(CH3)-COO-.

The preferred Z amine functions are chosen from among the secondary or tertiary amine functions contained in a cyclic hydrocarbon chain having the following formula:

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- the R<sup>9</sup> radicals, which may be identical or different from one another, are chosen from among the linear or branched alkyl radicals having from 1 to 3 carbon, phenyl and benzyl atoms,
- R<sup>10</sup> is chosen from among a hydrogen atom, linear or branched alkyl radicals having from 1 to 12 carbon atoms, alkylcarbonyl radicals where the alkyl remainder is a linear or branched remainder having from 1 to 8 carbon

atoms, the phenyl and benzyl radicals and an O- radical;

- h is a number chosen from among 0 and 1.

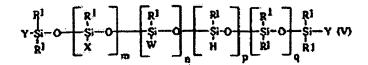
More preferably, the Z amine functions are chosen from among those of formula (IV) in which the  $R^9$  radicals are methyls, the  $R^{10}$  radical represents a hydrogen atom or a methyl radical and h is a number equal to 1.

The preferred W compatibilizing functions are chosen: from among a linear or branched alkyl radical having from 11 to 30 carbon atoms; a radical of formula  $-R^3$ -COO- $R^4$  in which  $R^3$  represents a linear or branched alkylene radical having from 8 to 12 carbon atoms and  $R^4$  represents a linear or branched alkyl radical having from 1 to 6 carbon atoms; a radical of formula  $-R^5$ -O- $(R^6$ -O)<sub>c</sub>- $R^7$  in which  $R^5$  represents a linear or branched alkylene radical having from 9 to 12 carbon atoms,  $R^6$  represents a linear or branched alkylene radical having from 2 to 3 carbon atoms, c is a number from 0 to 6 and  $R^7$  represents a hydrogen atom, a linear or branched alkyl radical having from 1 to 6 carbon atoms or an acyl radical -CO- $R^8$  where  $R^8$  represents a linear or branched alkyl radical having from 1 to 3 carbon atoms.

More preferably, the W compatibilizing functions are chosen from among the radicals n-undecyl, n-dodecyl, n-tridecyl, and decamethylene carboxylate of methyl or ethyl.

The primary object of this invention is more specifically the following:

- mixed, linear, statistical, sequenced or block polydiorganosiloxane copolymers having the following average formula:



#### wherein:

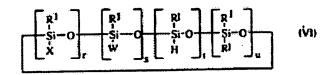
- symbols  $R^1$ , X and W have the general meanings given above with regard to formulas (I) and (II);
- the Y symbols represent a monovalent radical chosen from among R1, /6
  X, W and a hydrogen atom;
- m is a whole number or fraction between 0 and 180
- n is a whole number or fraction between 0 and 180
- p is a whole number or fraction between 0 and 10
- q is a whole number or fraction between 0 and 100;
- with the following conditions applying:
- if m and n are different from 0: the sum m + n + p + q shall fall within the range of 5 to 200; the ratio 100 m / m + n + p + q  $\geq$  0.5; and the ratio 100 n / m + n + p + q + 2  $\geq$  0.5, this ratio being identical to or different from

#### the previous ratio;

- if m = 0 and n is different from 0: at least one of the Y substituents represents the X radical; the sum m + n + p + q falls within the range of 5 to 100; and the ratio 100 n / m + n + p + q + 2  $\geq$  0.5;
- if m is different from 0 and n = 0: at least one of the Y substituents represents the W radical; the sum m + n + p + q falls within the range of 5 to 100; and the ratio 100 m / m + n + p + q + 2  $\geq$  0.5; and
- if m = 0 and n = 0: the sum p + q falls within the range of 5 to 100;

one of the Y substituents being the X radical; and the other Y substituent being the W radical;

and those having the following average formula:



#### wherein:

- the symbols R<sup>1</sup>, X and W have the general meanings given above with regard to formulas (I) and (II);
- r is a whole number or fraction between 1 and 9;
- s is a whole number or fraction between 1 and 9;
- t is a whole number or fraction between 0 and 0.5;
- u is a whole number or fraction between 0 and 5;
- the sum r + s + t + u falls within the range of 3 to 10.

Polymers of formula (V) which are either preferable (polymers called PL1) or highly preferable (polymers called PL2), are those for which the following applies:

- \* according to a first modality:
- the Y symbols represent R<sup>1</sup>;
- m is a whole number or fraction between 1 and 90
- n is a whole number or fraction between 1 and 90
- p is a whole number or fraction between 0 and 5
- q is a whole number or fraction between 0 and 50;

- the sum m + n + p + q is a whole number or fraction between 0 and 100;
- the ratio 100 m / m + n + p + q + 2 falls within the range of 10 to 90;
- the ratio 100 n / m + n + p + q + 2 falls within the range of 10 to 90, this ratio being identical to or different from the previous ratio;
- radicals R1, X and W simultaneously have the definitions of preferable (in the case of PL1 polymers) or highly preferable (in the case of PL2 polymers) given above respective to each one;
- \* according to a second modality:
- m = 0 and n = 0;
- one of the Y substituents is the radical X, while the other Y substituent
   is the radical W;
- p = 0;
- q is a whole number or a fraction between 5 and 10;
- radicals R1, X and W simultaneously have the definitions of preferable (in the case of PL1 polymers) or highly preferable (in the case of PL2 polymers) given above respective to each one;

Polymers of formula (VI) which are preferable (polymers called PC1) or highly preferable (polymers called PC2) are those for which:

- r is a whole number or fraction between 1 and 4.5;
- s is a whole number or fraction between 1 and 4.5;
- ullet t is a whole number or fraction between 0 and 0.25;
- u is a whole number or fraction between 0 and 2.5;
- the sum r + s + t + u falls within the range of 3 to 5;
- radicals R1, X and W simultaneously have the definitions of preferable

(in the case of PL1 polymers) or highly preferable (in the case of PL2 polymers) given above respective to each one.

Advantageously, the mixed organopolysiloxanes per the invention with oxygen hinge can be obtained from the following, being the first modality of the second object of the invention:

- corresponding organohydrogenpolysiloxanes (H) which have no Z amine function(s) having the oxygen hinge and W compatibilizing functions,
- of hydroxylated organic compound(s) ( $\psi$ ) from which the Z amine /8 function(s) of the oxygen hinge are derived,
- of ethylenically unsaturated compounds at the end of chain  $\Xi$  from which the W functions are derived.
- Thus the mixed polyorganisiloxanes as claimed in the invention can be obtained by the simultaneous dehydrocondensation reaction and addition (hydrosilylation) or preferably by reactions of dehydrocondensation then successively addition (hydrosilylation), from the following: organohydrogenpolysiloxanes (H) having no Z functions, having the oxygen hinge and W, hydroxylated organic compound(s) (\psi) from which the Z amine function(s) having the oxygen hinge are derived, and ethylenically unsaturated compound(s) at the end of the chain (\(\mathbb{E}\)) from which the W functions are derived.

These dehydrocondensation and hydrosilylation reactions can be carried out at a temperature on the order of 20 to 200°C, preferably on the order of 60 to 120°C, in the presence of a metal-based catalyst from the platinum group; in particular we cite the derivatives and complex of platinum described in US-A-3 715 334, US-A-3 814 730, US-A-3 159 601

and US-A-3 159 662.

The amounts of catalyst used are on the order of 1 to 300 parts per million, expressed as metal in relation to reaction medium.

In the definition of "mole of  $(\psi)$ " we shall consider as an elementary entity the OH function which is able to react with (H) by dehydrocondensation. Likewise in the definition of the "mole of  $(\Xi)$ " we shall consider as an elementary entity the olefin unsaturation that can react with (H) by hydrosilylation.

The amounts of reagents that can be used generally correspond to a molar ratio [( $\Xi$ ) + ( $\psi$ )]/SiH [of (H)] which is on the order of 1 to 5, preferably on the order of 1 to 2.

The dehydrocondensation and hydrosilylation reactions may take place in a mass or preferably in a volatile organic solvent such as toluene, xylene, methylcyclohexane, tetrahydrofurane, heptane, octane or isopropanol; the reaction medium may also contain a buffer agent consisting in particular in an alkaline salt of a monocarboxylic acid such as for example sodium acetate.

When the reactions have ended, the mixed raw polyorganosiloxanes obtained can be purified, in particular by passing them through a column filled with an ion exchange resin and/or by simple devolatilization of the reagents introduced in excess and possibly of the solvent used, by heating carried out between 100 and 180°C under reduced pressure.

The organohydrogenpolysiloxanes (H) serving for example for

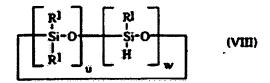
preparation of cyclic mixed polydiorganosiloxanes of formula (V) are those having the following formula:

$$Y = \begin{cases} R^1 & R^1 \\ Y = Si - O \\ R^1 & R^1 \end{cases} \qquad \begin{cases} R^1 & R^1 \\ Si - O \\ R^1 & R^1 \end{cases} \qquad (VIII)$$

wherein:

- symbols R<sup>1</sup> and q have the general or preferred meanings given above with regard to formula (V):
- symbols Y' represent R<sup>1</sup> or a hydrogen atom;
- v is a whole number or a fraction equal to m + n + p;
- with the condition that, if v = 0, then q is a number in the range from 5 to 100 and the two Y' radicals represent a hydrogen atom.

The organohydrogenpolysiloxanes (H) serving for example for preparation of cyclic mixed polydiorganosiloxanes of formula (VI) are those having the following formula:



- The symbols R<sup>1</sup> and u have the general or preferred meanings given above with regard to formula (VI);
- w is a whole number or a fraction equal to r + s + 1;
- the sum u + w falls within the range of 3 to 10.
   These organohydrogenpolysiloxanes (H) of formulas (VII) and (VIII)

are known in the literature and some of them are commercially available.

The hydroxylated organic compounds ( $\psi$ ) from which the Z functions having the oxygen hinge are derived (or also: from which the monovalent groups X are derived) are preferably of the following formula:

$$HO \xrightarrow{CH_2 \atop h} R^9 R^9 \qquad (IX)$$

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in which the symbols  $R^9$ ,  $R^{10}$  and h have the general or preferred meanings given above with regard to formula (IV).

As  $(\psi)$  compounds we can cite the following for example: hydroxy-4-tetramethyl-2,2,6,6-piperidine, hydroxy-4-pentamethyl-1,2,2,6,6-piperidine.

The unsaturated compounds (E) from which the W functions are derived are compounds having an ethylene unsaturation located at the end of the chain, which can react in hydrosilylation in the presence of a metal-based catalyst from the platinum group.

As (E) compounds we can cite the following for example: undecene-1, dodecene-1, tridecene-1, undecenoate of methyl or ethyl.

Advantageously, the mixed organopolysiloxanes per the invention with carboxylate hinge may be obtained from, and this contributes to a second modality of the second object of the invention:

- Corresponding organohydrogenpolysilanes (H) with no Z amine function(s)
   having the carboxylate hinge and W compatibilizing functions,
- of hydroxylated organic compound(s) (ψ) from which the Z amine function(s)
   of the carboxylate hinge are derived,

• of ethylenically unsaturated compounds at the end of chain (E) from which the W functions are derived.

Thus, the mixed polyorganosiloxanes as claimed in the invention can be obtained by the reactions of simultaneous or successive additions (hydrosilylations) of the following: corresponding organohydrogenpolysiloxanes (H) having no Z functions, having the carboxylate hinge and W, hydroxylated organic compound(s) ( $\psi$ ) from which the Z amine function(s) having the carboxylate hinge are derived, and ethylenically unsaturated compound(s) at the end of the chain ( $\Xi$ ) from which the W functions are derived.

These simultaneous or successive hydrosilylation reactions can be carried out under the same operating conditions (in particular: type and amount of catalyst; reaction temperatures; type of optional solvents) as those described above within the framework of dehydrocondensation reactions and additions that come into play for preparation of mixed polyorganosiloxanes with an oxygen hinge.

According to one preferred modality, said simultaneous or successive hydrosilylation reactions are carried out in the presence of a radical polymerization inhibiting agent chosen from among the following in particular: alkylated or alkoxylated monophenols [such as for example para-methoxyphenol, bis(ditertiobutyl-3,5-hydroxy-4-phenyl) methane and mixtures thereof]. The weighted quantity of an agent such as this, expressed in relation to the weight of the reaction medium, is in general between 0.001% and 0.1%.

In the definition of "mole of  $(\psi)$ " we shall consider here as an

elementary entity the olefin unsaturation which is able to react with (H) by hydrosilylation; the molar ratio  $[(\psi') + (\Xi)/SiH [of (H))]$  varies there too between 1 and 5 and preferably between 1 and 2.

The unsaturated organic compounds ( $\psi'$ ) from which the Z functions having the carboxylate hinge derive (or also: from which the monovalent X groups derive) are preferably those having the following formula:

$$CH_{2} = C - COO - CH_{2} + R^{9} R^{9}$$

$$CH_{2} + R^{10} R^{9}$$

$$CH_{3} + R^{9} R^{9}$$

$$CH_{3} + R^{9} R^{9}$$

wherein the symbols  $R^2$ ,  $R^9$ ,  $R^{10}$  and h have the general or preferred meanings given above with regard to the definition of the symbol X and formula (IV).

As compounds ( $\psi'$ ) we can cite the following by way of examples: tetramethyl-2,2,6,6-piperidinyl-4 methacrylate, pentamethyl-1,2,2,6,6-piperidinyl-4 methacrylate. These compounds are known in the literature (see in particular W. LAU et al., J. Polym. Sci. Part A: Polym. Chem., 30 (1992) pages 983 and subsequent) and they can be prepared by reaction of the piperidinol compounds on the methyl (meth) acrylate in the presence of a catalyst based on a metal alcoholate.

The mixed polyorganisiloxanes as claimed in the invention can be used as stabilizers against oxidizing light and heat degradation of organic polymers, and this constitutes the third object of the invention.

Examples of these organic polymers are polyolefins, polyurethanes,

polyamides, polyesters, polycarbonates, polysulfones, polyether-sulfones, polyether-ketones, acrylic polymers, their copolymers and mixtures thereof.

Among these polymers, the compounds as claimed in the invention have a more particularly effective action with the polyolefins and polyalkadienes such as polypropylene, high-density polyethylene, linear low-density polyethylene low-density polyethylene, polybutadiene, their copolymers and mixtures thereof.

Taking into account the many possibilities for variations of /12 the relative numbers of the different siloxyl units present in the siloxane chain of mixed compounds as claimed in the invention, these compounds can easily be adapted to the different problems to be resolved.

Another object of this invention therefore consists in organic polymer compositions stabilized against the detrimental effects of heat and UV by an effective quantity of at least one mixed polyorganosiloxane compound.

Usually these compositions contain from 0.04 to 20 milliequivalents in sterically hindered amine function(s) for 100 g of polymer to be stabilized.

Preferably the stabilized polymer compositions as claimed in the invention contain from 0.20 to 4 milliequivalents in sterically hindered amine function(s) for 100 g of polymer.

By way of example, generally the stabilized polymer compositions contain from 0.01% to 5% by weight of mixed polyorganosiloxane in relation to the polymer.

The addition of mixed polyorganosiloxane compounds can be done during or after preparation of polymers.

These compositions may also contain all the additives and stabilizers used conventionally with the polymers that they contain. Thus the following stabilizers and additives can be used: antioxidants as alkylated monophenols, alkylated hydroquinones, hydroxylated diphenyl sulfides, alkyldiene-bis-phenols, benzyl compounds, acylamino phenols, esters or amides of (di-tertiobutyl-3,5-hydroxy-4-phenyl)-3 propionic acid, (dicyclohexyl-3,5-hydroxy-4-phenyl)-3 propionic acid esters; light stabilizers such as possibly substituted benzoic acid esters; acrylic esters, nickel compounds, oxalamides, phosphites and phosphonites, metal deactivators, peroxide destruction compounds; polyamide stabilizers; nucleation agents; boosters and strengthening agents; other additives such as for example plastifiers, pigments, optical bleaches, fire retardants.

The compositions of polymers stabilized in this manner can be applied in the most varied forms, for example in the form of molded objects, leaves, fibers, porous materials (foam), slabs or coating products or as film-forming agents (binders) for paints, varnishes, glues or cements.

The following examples illustrate this invention.

In these examples, theoretical concentration of Z amine functions, expressed in milliequivalents (meq) for 100 g of silicone oil, shall mean the concentration that silicone oil would have if all the amine functions involved were grafted.

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#### Example 1

# Example of preparation of a mixed organopolysiloxane with oxygen hinge

The following are added to a 250 cm³ reactor equipped with a central mixing system and having an internal volume kept in an atmosphere of dry nitrogen: 25 g (0.159 moles) of hydroxy-4-tetramethyl-2,2,6,6-piperidine, 100 cm³ of dry toluene, 0.01 g of sodium acetate and 22 nm³ (or  $\mu$ l) of a solution, in divinyltetramethyldisiloxane, of a platinum complex having 12% by weight of platinum liganded by divinyltetramethyldisiloxane (Karstedt catalyst).

The reaction medium is brought to 100°C, and then 20 g of a polymethylhydrogensiloxane oil (i.e., 0.316 moles of Si-H functions) having the following characteristics is progressively poured in over a period of 3 hours:

- Mn = 3160 q;
- 1580 meg. H/100 g;
- average structure:

After having poured the oil with hydrogen silyl functions for 3 hours, the reaction medium is left to react at 100°C for 24 hours. At the end of this time, 34% of the hydrogen silyl functions (by mole) have been converted.

Then, 75 g (0.44 moles) of 95% by weight dodecene-1 is progressively added by pouring over a period of one hour. After the dodecene has been poured, the reaction medium is left to react at 100°C for 8 hours. All

of the hydrogen silyl functions should have been converted by now.

The reaction medium is cooled to ambient temperature  $(23^{\circ}\text{C})$ , then washed by extraction with  $100~\text{cm}^3$  of water. The residual organic phase is concentrated using a rotating evaporator, heating to  $160^{\circ}\text{C}$  under reduced pressure of  $0.67 \cdot 10^2$  Pa for 3 hours. 65 g of a clear oil is thereby recovered, having the following characteristics:

- Mn = 11300 g;
- 178.5 Meq of Z amine functions / 100 g, for a theoretical 222 meq/100 g (this index of basicity is measured by titration of the oil obtained using a perchloric acid solution 0.02 N);

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• average structure of oil:

- proportion of Z functions: 38.5% (by moles of functions for 100 atoms of silicon);
- proportion of W functions: 57.5%.

#### Example 2

Example of preparation of a mixed organopolysiloxane with oxygen hinge

The following are added to a  $250~{\rm cm}^3$  reactor equipped as described in Example 1:  $27.3~{\rm g}$  (0.159 moles) of

hydroxy-4-pentamethyl-1,2,2,6,6-piperidine and 100 cm3 of toluene

containing 0.012 g of sodium acetate. In two measures, add 60  $nm^3$  (or  $\mu$ l) of the Karstedt catalyst solution described in Example 1.

The reaction medium is brought to 90°C, and then 20 g of a polymethylhydrogensiloxane oil as described in Example 1 (i.e., 0.316 moles of Si-H functions) is progressively poured in over a period of 3 hours.

After having poured in the oil with hydrogen silyl functions for a period of 3 hours, the reaction medium is left to react at 90°C for 24 hours. At the end of this time, 44.3% of the hydrogen silyl functions (by mole) have been converted.

Then, 60 g (0.356 moles) of 95% by weight dodecene-1 is progressively added by pouring over a period of one hour. After the dodecene has been poured, the reaction medium is left to react at 100°C for 6 hours. All of the hydrogen silyl functions should have been converted by now.

Then 2 g of Amberlite A21 brand commercially available ion exchange resin is added and the reaction medium is allowed to cool at  $80^{\circ}\text{C}$  for 3 hours then filtered onto a milliport membrane (porosity of 0.2  $\mu\text{m}$ ). The product obtained is then devolatilized for 2 hours at  $160^{\circ}\text{C}$  under reduced pressure of  $0.67\cdot10^2$  Pa for 3 hours. 32 g of a clear oil is thereby recovered, having the following characteristics:

- Mn = 11300 g;
- 197.8 meq of Z amine functions / 100 g, for a theoretical 219 meq/100 g
- average structure of the oil:

- proportion of Z functions: 42.3% (by moles of functions for 100 atoms of silicon);
- proportion of W functions: 53.7%.

#### Example 3

Example of preparation of a mixed organopolysiloxane with carboxylate hinge

#### 1) Preparation of tetramethyl-2,2,6,6 piperidinyl-4 methacrylate

The following are added to a 250 cm³ reactor equipped with a mechanical central mixing system, a thermometer and a thermally insulated distillation column 45 cm high, the following is added: 0.6 g (0.024 moles) of magnesium, then the upper part of the reactor purged with nitrogen; then 10 cm³ of dry methanol and 0.5 g of dibromo-1,2-ethane. The reaction medium is brought to 45°C, and hydrogen and magnesium dimethoxylate form.

Once the hydrogen has been released, add 40 g (0.25 moles) of hydroxy-4-tetramethyl-2,2,6,6-piperidine, then 142 g (1.42 mole) of methyl methacrylate (mass titer: 99.8%), and the reaction medium is brought to its reflux temperature. The methanol formed distills.

Once the distillation of methanol has ended, the reaction medium is allowed to cool to ambient temperature (23°C), then poured into

660 cm<sup>3</sup> of water. The mixture obtained is filtered onto Kieselguhr-type earth commercially available under the name of Clarcel DIT 2R. The two phases are separated and the aqueous phase is extracted by 3 times 200 cm<sup>3</sup> of methyl methacrylate. After washing of all the organic phases with 50 cm<sup>3</sup> of water and drying on  $Na_2SO_4$ , the organic medium is concentrated using a rotating evaporator. In this way, 55.3 g of a light yellow solid is recovered (yield of isolated product: 88.6% by weight in relation to the amount of piperidinol involved).

The solid product obtained is recrystallized using a mixture of 20 cm<sup>3</sup> acetone with 10 cm<sup>3</sup> of water. After drying at ambient temperature (23°C) under 1.33 · 102 Pa, 49.1 g of white solid is recovered whose melting point is 60°C (measured by DSC analysis). The yield of recrystallized product is 80%. RMN and infrared analyses will confirm the expected structure of the product.

# 2) Preparation of the mixed organopolysiloxane:

The following are added to a 50 cm<sup>3</sup> reactor equipped with a mixing system and having an internal volume kept in an atmosphere of dry nitrogen: 13.6 g of dry toluene and 0.003 g of sodium acetate which is brought to  $110^{\circ}$ C, and then  $4.5 \text{ nm}^{3}$  (4.5 µl) of the Karstedt catalyst solution described in Example 1 is added.

Then, simultaneously, over a period of 80 minutes, and while keeping the temperature at 110°C, a solution of 12.88 g (0.057 mole) of tetramethyl-2,2,6,6-piperidinyl-4 methacrylate and 0.1 g of paramethoxyphenol in 9.5 nm³ of dry toluene and on the other hand 5.25 g of the polymethylhydrogensiloxane oil used in Example 1 (0.083 mole

of Si-H functions).

After having poured the oil, it can be observed that the conversion rate of hydrogen silyl functions is 70%. Then once more 4.5 nm³ (4.5 µl) of the Karstedt catalyst solution described in Example 1 is added and progressively over a period of 20 minutes, 8.13 g (0.048 mole) of 95% by weight of dodecene-1 is also added, while keeping the temperature at 110°C. After pouring the dodecene, the reaction medium is left to react for 6 hours at 110°C. At the end of this time, the conversion rate of hydrogen silyl functions is 100%.

The product obtained is then devolatilized for 3 hours at 138°C under reduced pressure of 0.399 10<sup>2</sup> Pa. Thus 20.12 g of a very light clear yellow liquid is obtained which has the following characteristics:

• Mn = 13420 g; /17

• 248.3 meq of Z amine functions/100 g for a theoretical 258 meq/100 g

$$\begin{array}{c} \text{CH}_{,})_{3}\text{Sio} = \begin{bmatrix} \text{CH}_{3} \\ \text{Si} = \text{O} \\ \text{CH}_{2} \\ \text{CH} = \text{CH}_{3} \\ \text{CH}_{33,3} \end{bmatrix} \begin{bmatrix} \text{CH}_{3} \\ \text{Si} = \text{O} \\ \text{Ci}_{12}\text{H}_{29} \end{bmatrix}_{16,7} \\ \text{CH}_{,} \\ \text{CH}_{3} \\ \text{CH}_{3} \\ \text{CH}_{3} \\ \text{CH}_{3} \\ \text{CH}_{3} \\ \end{array}$$

- average structure of the oil:
- moreover, nuclear magnetic resonance reveals the presence of 3.3% by mole of T units;

- proportion of Z functions: 64% (in moles of functions for 100 atoms of silicon);
- proportion of W functions: 32%

#### Example 4

Example of preparation of a mixed organopolysiloxane with carboxylate hinge

# 1) Preparation of pentamethyl-1,2,2,6,6 piperidinyl-4 methacrylate

The following is added to a 500 cm<sup>3</sup> five-neck reactor equipped with a mechanical central mixing system, a thermometer and a thermally insulated distillation column 45 cm high: 0.93 g (0.038 mole) of magnesium, then the upper part of the reactor purged with nitrogen; then 15 g of anhydrous methanol is added.

The reaction medium is brought to 45°C, and hydrogen and magnesium dimethoxylate form. Once the hydrogen has been released, add:

- 69.2 g (0.404 moles) of hydroxy-4-pentamethyl-1,2,2,6,6-piperidine (mass 97% pure), then
- 217 g (2.17 moles) of methyl methacrylate (mass 99.8% pure),
- 2.17 g of bis (3,5-ditertiobutyl-4-hydroxyphenyl) methane and the reaction medium is brought to its reflux temperature. The methanol formed distills for about two hours. The heating is then stopped. When the temperature has gone down to 40°C, 5 cm³ of distilled water is poured in while mixing.

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A precipitate is formed which is filtered, then the organic phase is dried on anhydrous sodium sulfate. Filtered again, the medium is then concentrated by evaporation of methyl methacrylate in the rotating

evaporator (80°C under 7.98  $\cdot$  10<sup>2</sup> Pa). From this concentrated medium, 56.7 g (0.233 mole) of 98% pure (mass) pentamethyl-1,2,2,6,6 piperidinyl-4 methacrylate is extracted by distillation under reduced pressure (75°C under 0.1  $\cdot$  10<sup>2</sup> Pa) in a Vigreux column 45 cm high.

# 2) Preparation of a mixed organopolysiloxane:

The following are added to a 50 cm<sup>3</sup> reactor equipped with a mixing system, thermometer and condenser:

- 6.9 g of dry toluene
- 0.0034 g of sodium acetate
- 2.2 mg of the Karstedt catalyst solution described in Example 1, and
- 0.05 g of bis(3,5-ditertiobutyl-4-hydroxyphenyl)methane

The contents of the reactor are brought to 108°C, and the top part of the reactor is rendered inert with nitrogen. Then simultaneously, over a period of 80 minutes, and while keeping the temperature at 108°C, using two separate syringes, the following is then poured:

- on the one hand:
- 15 g (0.062 mole) of the 98% pure pentamethyl-1,2,2,6,6 piperidinyl-4 methacrylate that resulted from Example 4 (part 1)
- 15 g of dry toluene,
- and on the other hand:
- 5.2 g (0.082 mole of Si-H functions) of the polymethylhydrogensiloxane oil used in Example 1.

Twice in the course of the reaction (2 hours, then 3 hours 30 minutes after the beginning of the reaction) add 2.2 mg of the Karstedt catalyst solution described in Example 1.

24 hours after the beginning of the reaction the conversion rate of the hydrogen silyl functions (in moles) is 71% (i.e., a conversion rate of pentamethyl piperidinyl methacrylate functions of 93%). Then 8 g (0.0474 mole) of 95% by weight dodecene-1 is injected over a period of 20 minutes, while keeping the temperature at 108°C.

4 hours after the injection of dodecine is finished, the conversion rate of the hydrogen silyl functions is 98.2%.

The product obtained is then devolatilized for 2 hours 30 minutes at 130°C under reduced pressure of 2.66 10² Pa. Thus 21.8 g of a light clear yellow liquid is obtained which has the following characteristics:

- Mn = 14110 g;
- 271.4 meg of Z amine functions/100 g of oil
- average structure of the oil:

- moreover, nuclear magnetic resonance reveals the presence of 15% by mole
   of T units;
- proportion of Z functions: 73.5% (by moles of functions for 100 atoms of Si);

• proportion of W functions: 20.8%.

#### Example 5

# Preparation of a mixed organopolysiloxane with carboxylate hinge

The following are added to a 50 cm<sup>3</sup> four-neck reactor equipped with a central mechanical mixing system, thermometer and condenser:

- 31.1 g of dry toluene
- 0.0034 g of sodium acetate, and
- 2.2 mg of the Karstedt catalyst solution described in Example 1.

The contents of the reactor are brought to 110°C, and the top part of the reactor is rendered inert with nitrogen.

Then simultaneously, over a period of 80 minutes, using two separate syringes, the following is then poured:

- on the one hand:
- 15 g (0.062 mole) of the 98% pure pentamethyl-1,2,2,6,6 piperidinyl-4 methacrylate that resulted from Example 4 (part 1)
- 15 g of dry toluene,
- 0.05 g of bis(3,5-ditertiobutyl-4-hydroxyphenyl)methane,

and on the other hand:

- 9.74 g (0.154 mole of Si-H functions) of the polymethylhydrogen siloxane oil used in Example 1.

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When all the pouring is done, the conversion rate of the hydrogen silyl functions (in moles) is 20.4%. Twice in the course of the reaction (3 hours, then 7 hours after the beginning of the reaction) add 2.2 mg of the Karstedt catalyst solution described in Example 1.

24 hours 30 minutes after the beginning of the reaction, the

conversion rate of the hydrogen silyl functions (in moles) is 27% (i.e., a conversion rate of pentamethyl piperidinyl methacrylate functions of 68%). Then the following is injected:

- 2.2 mg of the Karstedt catalyst solution described in Example 1.
- 31.1 g (0.184 mole) of 95% by weight dodecene-1 over a period of 20 minutes while keeping the temperature at 110°C.

5 hours 30 minutes after the dodecene has been injected, the conversion rate of the hydrogen silyl functions is 94.4%.

The product obtained is then devolatilized for 2 hours and 30 minutes at  $140^{\circ}$ C under a reduced pressure of  $2.66 \cdot 10^{2}$  Pa. 35.3 g of a clear yellow oil is recovered which has the following characteristics:

- Mn = 12000 q;
- 106.2 meq of Z amine functions/100 g of oil
- average structure of the oil:

(CH<sub>3</sub>), SiO 
$$\begin{bmatrix} CH_1 \\ SI - O \\ SI - O \end{bmatrix}$$
  $\begin{bmatrix} CH_2 \\ SI - O \\ SI - O \end{bmatrix}$   $\begin{bmatrix} CH_3 \\ SI - O \\ SI - O \end{bmatrix}$   $\begin{bmatrix} CH_3 \\ SI - O \\ SI - O \end{bmatrix}$   $\begin{bmatrix} CH_3 \\ SI - O \\ SI - O \end{bmatrix}$   $\begin{bmatrix} CH_3 \\ SI - O \\ SI - O \end{bmatrix}$   $\begin{bmatrix} CH_3 \\ SI - O \\ SI - O \end{bmatrix}$   $\begin{bmatrix} CH_3 \\ SI - O \\ SI - O \end{bmatrix}$   $\begin{bmatrix} CH_3 \\ SI - O \\ SI - O \end{bmatrix}$   $\begin{bmatrix} CH_3 \\ SI - O \\ SI - O \end{bmatrix}$   $\begin{bmatrix} CH_3 \\ SI - O \\ SI - O \end{bmatrix}$   $\begin{bmatrix} CH_3 \\ CH_3 \\ CH_3 \end{bmatrix}$   $\begin{bmatrix} CH_3$ 

- moreover, nuclear magnetic resonance reveals the presence of 3.4% by mole of T units;
- proportion of Z functions: 24.4% (by moles of functions for 100 atoms of Si);

• proportion of W functions: 66.3%.

### Example 6

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# Light-stabilization of polypropylene (PP)

### Preparation of compositions:

- mixing 3 minutes at 160°C of 100 parts by weight of PP ELTEX® PHV001P
   (grade 10) + 0.2 part of a commercial antioxidant (see definition below)
  + 0.1 part of calcium stearate + 0.2 part stabilizer;
- compression under a platen press at 190°C (1 minute of contact + 1 minute holding at 250 105 Pa + 1 minute cooling at the same pressure).

Thus quasi-circular plates are obtained 200 micrometers think from which the specimens are cut out.

Control composition: stabilizer = CHIMASORB 944 (see formula below) containing 341 meg of piperidinyl functions for 100 g of stabilizer.

Compositions b, c, d and e: stabilizers = silicone oils described in Examples 1, 3 (part 2), 4 (part 2) and 5, respectively.

Definition of the commercial antioxidant used: 50/50 mixture by weight of pentaerythrityl

tetrakis(hydroxy-4'-ditertiobutyl-3',5'-phenyl)-3 propionate (sold under the name IRGANOX® 1010) and tris(ditertiobutyl-2,4-phenyl) phosphite (sold under the name IRGAFOS® 168).

Formula of the CHIMASORB® 944:

Compositions b and c were tested under UV B and compositions d and e under UV A. The control composition a was tested under UV A and UV B to serve as a comparison.

The progress of the degradation under UV B was observed using infrared spectrometry. Every two days until the film broke measurements were taken of the increase in absorbency (abbreviated A2) of the band of carbonyls at 1720 cm $^{-1}$  resulting from degradation of PP and this absorbency was brought to the absorbency (abbreviated A1) of a band of an inert group (methylene at 2722 cm $^{-1}$ ).

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·		A2	Concentration en tonctions amines (m6q/100 g d'huile)			
Composition	2 jours	4 jours	6 jours	8 jours	9 jours	
a	0.054	0.068	0,13	rupture		341
b	0,075	0.076	0.07	0.08	niphire	197,8
С	0.058	0.046	0.08	0.09	rupture	248.3

Key:

composition		concentration of amine functions (meq/100 g of oil)				
	2 days	4 days	6 days	8 days	9 days	
				breakage		
				[of film]		1
					breakage	
					[of film]	
					breakage	
					[of film]	

Under UV A, since the degradation was much slower than under UV B, the stabilizatio test was carried out by simply comparing the durations (D) after which the specimens broke. For each composition, three specimens were tested.

Composition et	<b>D</b> u	•	re de l'éproui heure)	Concentration on fonction amines (meg/100 g (Thuile)	Dinombre de még/100 g	
	éprouv.1	eprouv.2	ергоци,3	moyenne		
-8	744	768	798	770	341	2.26
đ	878	1198	1198	1090	271,4	4.02
ŧ	603	720	727	683	106.2	8.43

Key:

	durations ( D (hours)	D) after whi	concentration of amine functions (meq/100 g of oil)	D/number of meq/100 g.		
composition	Specimen 1	Specimen 2	Specimen 3	average		

CLAIMS /23

- 1. Mixed polyorganosiloxane wherein it comprises, per molecule, at least 3 siloxyl units including:
- at least one functional siloxyl unit having the formula:

$$(R^{j})_{a} \times Si(0)_{\underline{3-a}}$$
 (I)

- symbols R<sup>1</sup> are identical or different and represent a monovalent hydrocarbon radical chosen from among the linear or branched alkyl radicals, having from 1 to 4 atoms of carbon and phenyl;
- the symbol X represents a monovalent group having formula -A-Z where:
- A is a divalent radical chosen from among an oxygen atom and a radical having formula -CH<sub>2</sub>-CHR<sup>2</sup>-COO- with R<sup>2</sup> being a hydrogen atom or an linear or branched alkyl radical having from 1 to 3 carbon atoms, the free valency of the carbon atom being bound to the silicon atom;
- the symbol Z represents a monovalent group whose free valency is borne by a carbon atom, having a secondary or tertiary amine function, contained in a cyclic hydrocarbon chain having from 8 to 30 carbon atoms, in which the two cyclic carbon atoms situated in positions  $\alpha$  and  $\alpha'$  in relation to the cyclic nitrogen atom do not contain a hydrogen atom;
- a is a number chosen from among 0, 1 and 2; and
- at least one other functional siloxyl unit having the following formula:

$$(R^{b})_{b}$$
WSi(O)<sub>3-b</sub> (II)

wherein

- symbols R<sup>1</sup> have the same meanings as those given above with regard to formula (I):
- the symbol W represents a monovalent group with a compatibilizing function chosen from among the following: an alkyl linear or branched radical having more than 10 carbon atoms; a radical having formula  $-R^3$ -COO- $R^4$  in which  $R^3$  represents an linear or branched alkylene radical having from 5 to 20 carbon atoms and  $R^4$  represents an linear or branched alkyl radical having from 1 to 12 carbon atoms; a radical having formula /24  $-R^5$ -O- $(R^6$ -O)<sub>c</sub>- $R^7$  in which  $R^5$  represents a linear or branched alkylene radical having from 3 to 15 carbon atoms,  $R^6$  represents a linear or branched alkylene radical having from 1 to 3 carbon atoms, is a number from 0 to 10 and  $R^7$  represents a hydrogen atom, a linear or branched alkyl radical having from 1 to 12 carbon atoms or an acyl radical -CO- $R^8$  where  $R^8$  represents a linear or branched alkyl radical having from 1 to 11 carbon atoms;
- b is a number chosen from among 0, 1 and 2.
  - 2. Polyorganosiloxane as claimed in Claim 1, wherein it may also contain at least one other siloxyl unit having the following formula:

$$(R)_{d}(H)_{e}Si(O)_{\underbrace{4-(d+e)}{2}}$$
 (III)

wherein:

 symbols R<sup>1</sup> have the same meanings as those given above with regard to formula (I):

- d is a number chosen from among 0, 1, 2 and 3;
- e is a number chosen from among 0 and 1;
- the sum d + e is at most equal to 3.
  - 3. Polyorganosiloxane as claimed in either of Claims 1 or 2, wherein the R<sup>1</sup> radicals are as follows: methyl, ethyl, n-propyl, isopropyl, n-butyl and the carboxylate hinge is chosen from among the divalent radicals -CH2-CH2-COO- and -CH2-CH(CH3)-COO-.
  - 4. Polyorganosiloxane as claimed in any of Claims 1 through 3, wherein the preferred Z amine functions are chosen from among the secondary or tertiary amine functions contained in a cyclic hydrocarbon chain having the following formula:

$$CH_{2} \xrightarrow{R^{0}} R^{0} \qquad (iV)$$

- the R<sup>9</sup> radicals, which may be identical or different from one another, are chosen from among the linear or branched alkyl radicals having from 1 to 3 carbon, phenyl and benzyl atoms,
- R<sup>10</sup> is chosen from among a hydrogen atom, linear or branched alkyl /25 radicals having from 1 to 12 carbon atoms, alkylcarbonyl radicals where the alkyl remainder is a linear or branched remainder having from 1 to 8 carbon atoms, the phenyl and benzyl radicals and an O- radical;
- h is a number chosen from among 0 and 1.
  - 5. Polyorganosiloxane as claimed in any of Claims 1 through 4, wherein the preferred W compatibilizing functions are chosen: from among a linear

or branched alkyl radical having from 11 to 30 carbon atoms; a radical of formula  $-R^3$ -COO- $R^4$  in which  $R^3$  represents a linear or branched alkylene radical having from 8 to 12 carbon atoms and  $R^4$  represents a linear or branched alkyl radical having from 1 to 6 carbon atoms; a radical of formula  $-R^5$ -O- $(R^6$ -O)<sub>c</sub>- $R^7$  in which  $R^5$  represents a linear or branched alkylene radical having from 9 to 12 carbon atoms,  $R^6$  represents a linear or branched alkylene radical having from 2 to 3 carbon atoms, c is a number from 0 to 6 and  $R^7$  represents a hydrogen atom, a linear or branched alkyl radical having from 1 to 6 carbon atoms or an acyl radical -CO- $R^8$  where  $R^8$  represents a linear or branched alkyl radical having from 1 to 3 carbon atoms.

- 6. Polyorganosiloxane as claimed in any of Claims 1 through 5, wherein it is chosen from among the following:
- mixed, linear, statistical, sequenced or block polydiorganosiloxane copolymers having the following average formula:

- symbols R<sup>1</sup>, X and W have the general meanings given above with regard to formulas (I) and (II);
- the Y symbols represent a monovalent radical chosen from among R1, X, W and a hydrogen atom;
- m is a whole number or fraction between 0 and 180
- n is a whole number or fraction between 0 and 180
- p is a whole number or fraction between 0 and 10

- q is a whole number or fraction between 0 and 100;
- with the following conditions applying:

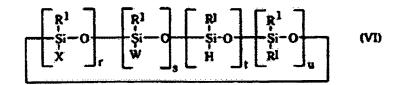
if m and n are different from 0: the sum m + n + p + q shall fall within the range of 5 to 200; the ratio 100 m / m + n + p + q  $\geq$  0.5; and the ratio 100 n / m + n + p + q + 2  $\geq$  0.5, this ratio being identical to or different from

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the previous ratio;

- if m = 0 and n is different from 0: at least one of the Y substituents represents the X radical; the sum m + n + p + q falls within the range of 5 to 100; and the ratio 100 n / m + n + p + q + 2  $\geq$  0.5;
- if m is different from 0 and n = 0: at least one of the Y substituents represents the W radical; the sum m + n + p + q falls within the range of 5 to 100; and the ratio 100 m / m + n + p + q + 2  $\geq$  0.5; and
- if m = 0 and n = 0: the sum p + q falls within the range of 5 to 100; one of the Y substituents being the X radical; and the other Y substituent being the W radical;

and those having the following average formula:



- the symbols R<sup>1</sup>, X and W have the general meanings given above with regard to formulas (I) and (II);
- r is a whole number or fraction between 1 and 9;
- s is a whole number or fraction between 1 and 9;

- t is a whole number or fraction between 0 and 0.5;
- u is a whole number or fraction between 0 and 5;
- the sum r + s + t + u falls within the range of 3 to 10.
  - 7. Polyorganosiloxane PL1 as claimed in claim 6, wherein:
- the Y symbols represent R<sup>1</sup>;
- m is a whole number or fraction between 1 and 90
- n is a whole number or fraction between 1 and 90
- p is a whole number or fraction between 0 and 5
- q is a whole number or fraction between 0 and 50;
- the sum m + n + p + q is a whole number or fraction between 0 and 100;
- the ratio 100 m / m + n + p + q + 2 falls within the range of 10 to 90;
- the ratio 100 n / m + n + p + q + 2 falls within the range of 10 to 90, this ratio being identical to or different from the previous ratio;

- radicals R1, X and W simultaneously have the definitions given above respective to each one of them I claims 3, 4 and 5.
  - 8. Polyorganosiloxane PC1 as claimed in Claim 6, wherein:
- r is a whole number or fraction between 1 and 4.5;
- s is a whole number or fraction between 1 and 4.5;
- t is a whole number or fraction between 0 and 0.25;
- u is a whole number or fraction between 0 and 2.5;
- the sum r + s + t + u falls within the range of 3 to 5;
- radicals R1, X and W simultaneously have the definitions given above respective to each one of them I Claims 3, 4 and 5.

- 9. Process for preparing a mixed polyorganosiloxane with oxygen hinge as claimed in any of Claims 1 through 8, wherein according to this process it is obtained by the reaction of dehydrocondensation and the simultaneous addition (hydrosilylation) or by reactions of dehydrocondensation and successive addition (hydrosilylation) of the following: corresponding organohydrogenpolysiloxanes (H) having no Z functions and having the oxygen hinge and W, hydroxylated organic compound(s) (\$\psi\$) from which the Z amine function(s) having the oxygen hinge are derived, and ethylenically unsaturated compound(s) at the end of the chain (\$\mathbrea\$) from which the W functions are derived, and wherein the reagents used correspond to a molar ratio of [(\$\psi\$) + (\$\mathbrea\$)/SiH [of (H)] which is on the order of 1 to 5.
- 10. Process for preparing a mixed polyorganosiloxane with carboxylate hinge as claimed in any of Claims 1 through 8, wherein according to this process it is obtained by the reaction of simultaneous or successive additions (hydrosilylations) of the following: corresponding organohydrogenpolysiloxanes (H) having no Z functions and having the carboxylate hinge and W, ethylenically unsaturated compound(s) at the end of the chain ( $\Xi$ ) from which the W functions are derived, and wherein the reagents used correspond to a molar ratio of  $[(\psi') + (\Xi)/SiH [of (H)]]$  which is on the order of 1 to 5.
- 11. Process as claimed in claim 9, wherein the hydroxylated organic compounds ( $\psi$ ) from which the Z functions having the oxygen hinge are derived (or also: from which the monovalent X groups are derived) are those having the following formula:

HO 
$$CH_{3} + R^{9}$$
 (1X)

wherein the symbols  $R^9$ ,  $R^{10}$  and h have the meanings given above with regard to formula (IV).

12. Process as claimed in claim 10, wherein the unsaturated organic compounds ( $\psi'$ ) from which the Z functions having the carboxylate hinge are derived (or also: from which the monovalent X groups are derived) are those having the following formula:

$$CH_{3} = C - COO - CH_{3} + R^{9} + R^{9}$$

$$CH_{3} = R^{9} + R^{9} +$$

wherein the symbols  $R^2$ ,  $R^9$ ,  $R^{10}$  and h have the meanings given above with regard to formula (IV).

- 13. Use of an effective amount of a mixed polyorganosiloxane as claimed in any of Claims 1 through 8, as stabilizers against the degradation effects of light, air and heat on organic polymers.
- 14. Use as claimed in Claim 13, wherein the organic polymers to be stabilized are chosen from among polyolefins, polyurethanes, polyamides, polyesters, polycarbonates, polysulfones, polyether-sulfones, polyether-ketones, acrylic polymers, their copolymers and mixtures thereof.
- 15. Organic polymer composition stabilized against the degradation effects of light, air and heat wherein it comprises the

### following:

- for 100 g of organic polymer to be stabilized
- a quantity of mixed polyorganosiloxane as claimed in any of claims 1 through 8 which contributes 0.04 to 20 milliequivalents in sterically hindered amine functions.
  - 16. Composition as claimed in Claim 15, wherein the organic polymers to be stabilized are chosen from among polyolefins, polyurethanes, polyamides, polyesters, polycarbonates, polysulfones, polyether-sulfones, polyether-ketones, acrylic polymers, their copolymers and mixtures thereof.